



# Considerations on the effect of solutal on the grain size of castings from superheated melts

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## ARTICLE INFO

### Article history:

Received 23 March 2017

Accepted 23 April 2017

Available online 25 April 2017

### Keywords:

Casting

Solidification

Grain refining

Phase diagram

Metal and alloys

## ABSTRACT

The amount of solutal present in an alloy affects the grain size of the cast metal as solute is rejected at the solidification front. This is normally quantified using the so called growth restriction factor  $Q$ . This work presents some considerations about the effect of solutal on the final cast structure with a focus on the nature of the alloy system, the effect of non-equilibrium solidification conditions and the effect of superheating of the molten metal.

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## 1. Introduction

The achievement of fine equiaxed grains is desirable in metals casting, independently of wrought or shape-casting alloys. Both grades benefit from better feeding of the molten metal in the mushy zone resulting in more homogeneously distributed porosity and reduced hot tearing susceptibility [1]. Apart increasing the soundness of the castings (i.e. lower rejection rate), other benefits of a fine structure are higher mechanical performances, and easier and more homogeneous subsequent mechanical working for wrought-grade alloys [2]. In every solidification process, metals casting involves nucleation of a new phase and consequent growth of the solid phase. Easton and StJohn reported that nucleation will not occur in the bulk of a metal without adequate solute being present [3]. The concept of *growth restriction factor* ( $Q$ ) was first introduced by Maxwell and Hellawell [4] as an independent parameter relevant to the refinement of cast structures, in particular for binary Al alloys.  $Q$  is an extension of the early work of Tarshis et al. [5] who proposed that the solute present in the solidification front accounts for the degree of growth restriction, a parameter that was called *constitutional supercooling parameter* ( $P$ ).  $Q$  and  $P$  are related via the equilibrium partition coefficient  $k$  [6]:

$$Q = m_L(k - 1)C_0 = kP \quad (1)$$

where  $m_L$  is the liquid slope, and  $C_0$  is the solute content in the alloy.

The scientific community focusing on solidification of molten metals has widely adopted the use of  $Q$  to relate it to the grain size ( $d$ ) of the casting [3,7] because otherwise complex thermodynamic models have to be implemented to study grain growth restriction [8,9]:

$$d = a + b/Q \quad (2)$$

In Eq. (2),  $a$  is a constant related to the number density of active nucleating particles, and  $b$  is a constant associated with the efficiency of the nucleating particles.

Although mainly used to quantify the effect of the presence of heterogeneous nuclei added to promote nucleation [3] (i.e. chemical inoculation), the relationship presented in Eq. (2) can also be used to study the effect of the solutal content on the grain size of the casting [3] where nucleation begins heterogeneously in the melt near the wall of the mould. It was shown that of the four contributions to the total undercooling (kinetic, curvature, thermal and solutal) the solutal or constitutional supercooling is the controlling term under typical Al alloys casting conditions [10]. Higher solutal content results in higher  $Q$  and finer grain size ( $d$ ) for commercial wrought Al alloys as shown in Fig. 1a (data from [3]). Nevertheless, the same relationship is not valid for shape-casting Al alloys based on the Al-Si system (Fig. 1b) (data from [11,12]).

A number of scientists have reported that as Si content initially increases, the Al solid solution grain size decreases. However, beyond a critical value (around 3 wt.% Si for typical Al alloys casting conditions) the grain size increases where this trend is

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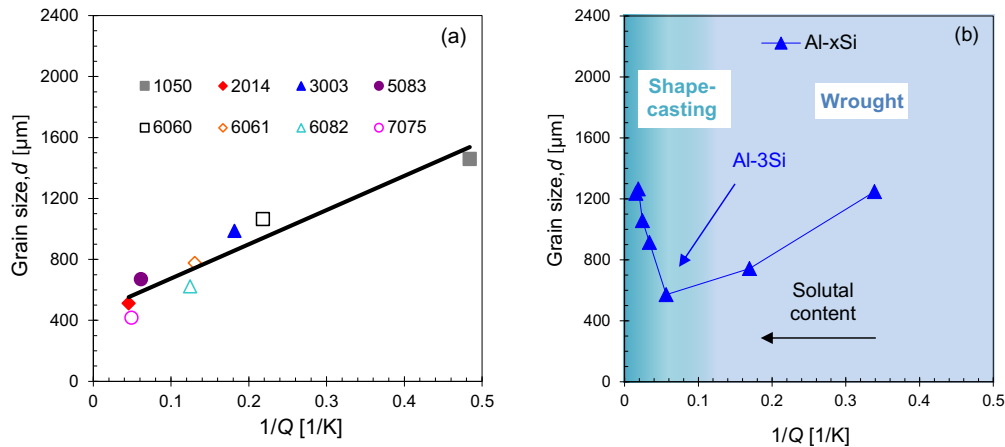


Fig. 1. Average grain size ( $d$ ) versus growth restriction factor  $Q$ . (a) Wrought Al alloys (data from [3]). (b) Shape-casting Al alloys (data from [11,12]).

observed both in grain refined and non-grain refined alloys, with the non-grain refined alloys exhibiting the coarser grains [12]. Although a number of explanations have been proposed such as change in crystal growth morphology [11] and Si poisoning [13] there is still debate about the real nature of this coarsening in non-refined Al-Si alloys. Moreover, it has been demonstrated via thermodynamic simulations that if Ti is present in excess to the amount needed to form nucleating  $\text{TiB}_2$  particles, the growth rate of Al dendrites in Al-Si alloys increases leading to grain coarsening [8,9].

The purpose of the work is to make some considerations about the effect of solutal content on the grain size of cast structure taking into account three aspects: (i) the nature of the alloy, (ii) the effect of non-equilibrium solidification conditions and (iii) the amount of superheating.

## 2. Consideration about the nature of the system

Arguably, one of the critical parameter influencing the final grain size is the total amount of solutal present in the alloy (i.e. smaller  $d$  for higher  $Q$ ) as it is accepted that solute is rejected by the growing grains upon solidification. However, the first important difference between the data presented in Fig. 1 is the intrinsic nature of the alloy system. In all the commercial wrought Al alloys, whose grain size is presented in Fig. 1a, the content of each of the solute elements, although high, it is never above the maximum solid solubility ( $C_{SM}$ ) of that specific element in Al (Table 1). These alloys are defined as *dilute alloy systems* in this work and in them the primary phase to nucleate is a solid solution of Al. For example, the 2014 alloy has an average content of 4.60 wt.% Cu, 0.52 wt.% Mg and 0.98 wt.% Si (these values are normally used in Eq. (1) as

$C_0$ ) and therefore one of the lowest  $1/Q$  and finer grain size in Fig. 1a. These solutal contents are lower than 5.65 wt.%, 17.10 wt.% and 1.65 wt.% which are the  $C_{SM}$  values for Cu, Mg and Si, respectively (Table 1). Although it was shown that the simultaneous presence of two or more solutes can change the primary forming phase [10], the principle of using  $C_{SM}$  seems to be still applicable in highly alloyed wrought Al alloys. In the case of shape-casting Al alloys (whose minimum Si content is approximately 5 wt.%) at equilibrium, off eutectic compositions solidify with a two-phase structure and are defined in this work as *two-phase alloy systems*. The fact that in shape-casting alloys  $C_0$  is greater than  $C_{SM}$  has implication which are discussed in the latter section jointly with the effect of non-equilibrium solidification conditions.

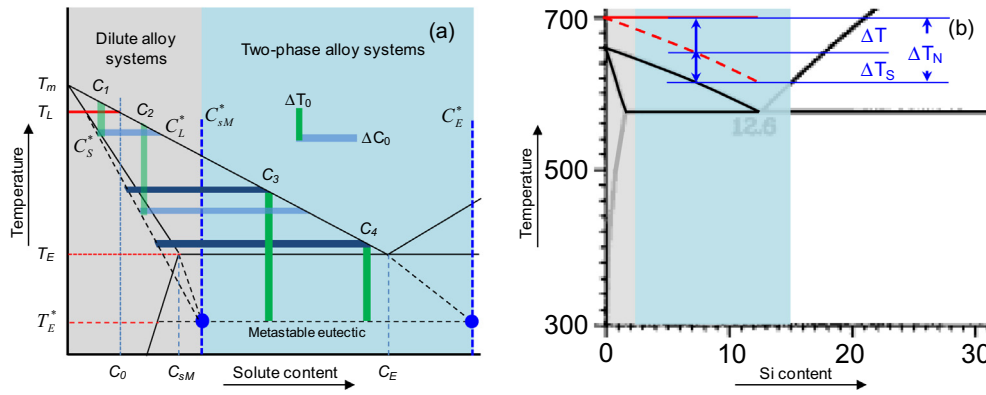
## 3. Consideration about non-equilibrium solidification conditions

Casting in practical instances, independently whether at industrial scale to fabricate products or at lab scale to study the nucleation and growth of crystals, does not happen under equilibrium conditions. This has direct implications on the equilibrium phase diagrams and on the cast structure. For example, it is well known that solidified grains have a cored structure, and thus microsegregation because the amount of solutal inside each grain increases as solidification progresses [15]. This justifies the eutectic phase being present in the cast structure of alloys whose solute content is much lower than the eutectic composition (i.e.  $C_E$ ). The non-equilibrium conditions should then be addressed using metastable phase diagram, an idealisation of which is presented in Fig. 2a. This means that under non-equilibrium solidification conditions the eutectic point is shifted to a higher solutal content (i.e.  $C_E^*$ ) and to

**Table 1**  
Solute content ( $C_0$ ) and maximum solid solubility ( $C_{SM}$ ) of different solute elements used in wrought and shape-casting Al alloys. Note: average  $C_0$  values are from [3] (for consistency) and  $C_{SM}$  values are from the corresponding binary phase diagrams [14].

Alloy		2014	5083	7075	Binary Al-xSi
Cu	$C_0$	4.60	–	1.69	–
	$C_{SM}$			5.65	
Mg	$C_0$	0.52	4.19	2.33	–
	$C_{SM}$			17.1	
Zn	$C_0$	–	–	5.22	–
	$C_{SM}$			16.5	
Si	$C_0$	0.98	0.35	0.28	1.0–11.0*
	$C_{SM}$			1.65	

\* Wrought Al alloys have a maximum Si content of 2 wt.% and shape-casting Al a minimum Si content of 5 wt.%; Si  $\sim 3$  wt.% is commonly used to discern them.



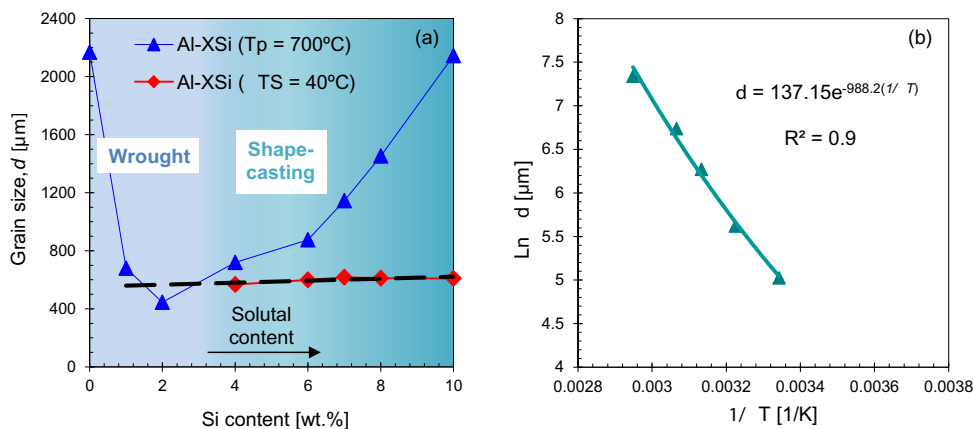
**Fig. 2.** Binary phase diagrams. (a) Sketch of an idealised equilibrium and metastable eutectic binary phase diagram. (b) Al-rich part of the eutectic binary Al-Si phase diagram [14].

lower temperature (i.e.  $T_E^*$ ). The maximum solubility point ( $C_{SM}^*$ ) is also virtually shifted to higher concentrations ( $C_{SM}^*$ ) and lower temperature. On the base of the data of Fig 1b, in the case of shape-casting Al-Si alloys  $C_{SM}^* = 1.8 \cdot C_{SM}$ .

Considering Fig. 2a,  $\Delta C_0$  is the composition range and  $\Delta T_0$  is the temperature range for each solutal content. The difference between the solutal content in the solid ( $C_S^*$ ) and in the liquid ( $C_L^*$ ) is  $\Delta C_0$  and they are used to define the equilibrium partition coefficient  $k$  of Eq. (1) (i.e.  $k = C_S^*/C_L^*$ ). The  $-\Delta T_0/\Delta C_0$  ratio then represents the liquidus slope  $m_L$  of Eq. (1). From Fig. 2a, it can be seen that two scenarios arises as solutal content increases depending on the intrinsic nature of the alloy system. On the one side,  $C_L^*$  and  $C_S^*$  increase proportionally and thus  $k$  remains constant for *dilute alloy systems*, such as compositions  $C_1$  and  $C_2$ , that are equivalent to wrought alloys. Moreover,  $\Delta C_0$  and  $\Delta T_0$  increase proportionally and therefore  $m_L$  is also approximately constant. On the other side,  $k$  remains constant but  $m_L$  continuously decreases, as  $\Delta C_0$  increases but  $\Delta T_0$  decreases with the solutal content, for *two-phase alloy systems* like compositions  $C_3$  and  $C_4$  (that correspond to shape-casting alloys). This is relevant because the parameters and theories proposed (i.e. Eqs. (1) and (2)) are based on the inherent assumptions that  $k$  and  $m_L$  are independent from the composition, and thus constant, as equilibrium is assumed to be maintained at the solid-liquid interface during solidification.

#### 4. Consideration about superheating

A survey of the literature about the effect of solutal on the grain size of cast structure of *dilute alloy systems* and *two-phase alloy systems*, that it is commonly studied jointly with the effect of chemical inoculation, indicates that different alloys are generally cast from constant temperature. This is done for the sake of simplicity and comparison. It is worth mentioning that in the case of Al alloys, chemical inoculation is normally done by means of the addition of Al-Ti-B master alloys. When the same alloy system is inoculated for grain refinement, the addition of free Ti is generally low (i.e. 0.005–0.02 wt.%) and thus it does not affect significantly the total superheating ( $\Delta T_N$ ) of the alloy (Fig 2b). Nonetheless, when alloys with different composition are compared, the total solutal amount determines  $\Delta T_N$ . This is especially relevant for scenarios like the one found in binary Al-xSi alloys where the total amount of Si is used to quantify the effect of solutal on the grain size (Fig. 1b) because  $\Delta T_N$  proportionally increases with the increment of Si content (Fig. 2b). To prove the importance of the effect of the total superheating, binary Al-XSi alloys, where  $X = 4$ –10 wt.%, were produced by mixing commercially pure Al (purity > 99.7%) with an Al-50Si master alloy. The alloys were melted at 800 °C during 2 h prior casting to check their composition; found to be within  $\pm 0.2$  wt.%. Pure Al and binary Al-XSi alloys were melted and cast either from



**Fig. 3.** Average grain size of binary Al-xSi alloy. (a) Grain size ( $d$ ) versus Si content for alloys cast from constant temperature ( $T_p = 700$ ) or with constant superheating ( $\Delta T_S = 40^\circ\text{C}$ ). (b) Logarithm of the difference in grain size ( $\Delta d$ ) vs  $1/\Delta T$ . The effect of the superheating on solidification can be represented with an Arrhenius-like equation because it is a diffusion-controlled process.

a constant pouring temperature  $T_p$  of  $700 \pm 3$  °C or with a constant superheating  $\Delta T_S$  of  $40 \pm 3$  °C at a constant cooling rate of 3.5 °C/s imposed by a water flow (i.e. TP-1 test [16]). Ground and polished samples were anodised in a  $\text{HBF}_4$  solution using a current of  $\sim 10\text{V}/1\text{A}$  to reveal the grains. Grain size measurements were done accordingly to ASTM E112 (intercept method) [17].

The data shown in Fig. 3a confirm the trend found by other scientists [11,12] when casting binary Al-XSi alloys from a constant temperature; the grain size initially decreases and then increases again. The decrement of the grain size happens for compositions lower than  $C_{SM}^*$  and thus for wrought-equivalent composition, whereas the increment is for compositions corresponding to shape-casting alloys. The casting of the binary Al-XSi alloy with constant superheating leads to a rather constant grain size independently of the Si content. It is worth noticing that even though Al-1Si and Al-2Si alloys where only cast from constant temperature, their  $\Delta T_S$  ( $\sim 50$  °C) is comparable to that used to cast alloys with much higher Si content from a constant superheating. Comparable final grain size are then roughly obtained as shown by the linear relationship in Fig. 3a.

Solidification of undercooled melts where equilibrium is kept at the solid-liquid interface is normally studied using Eq. (3) [18]:

$$k_S \cdot T'_S - k_L \cdot T'_L = v \cdot L_v \quad (3)$$

where  $k_S$  and  $k_L$  are the thermal conductivities of the solid and liquid phase respectively,  $T'_S$  and  $T'_L$  the temperature gradients,  $v$  is the growth velocity and  $L_v$  is the latent heat. Considering the case where the left-hand term of Eq. (3), which is related to the thermal gradient, it is supposed to remain constant because imposed by the constant cooling rate and the thermal conductivity, the grain size is dependent on the pouring temperature. For constant superheating, the amount of heat to be extracted from the molten metal is constant, and so it is the  $v \cdot L_v$  product. Conversely, for a constant pouring temperature the total amount of heat to be extracted upon solidification is proportionally higher for higher Si contents as the molten metal acts as a heat reservoir allowing more time for the nucleated grains to growth. Conduction and convection are expected in this scenario, and a basic thermodynamics analysis of heat exchange indicates that for both mechanisms the heat transferred per unit time is proportional to  $\Delta T_N$ . The variation of the difference in grain size between the alloys cast at constant temperature and those cast from constant superheating ( $\Delta d$ ) vs  $1/\Delta T$  has an Arrhenius-like behaviour (Fig. 3b) as solidification is a diffusive process:

$$\Delta d = A \cdot e^{-\frac{E_a}{R\Delta T}} \quad (4)$$

where the pre-exponential constant  $A$  is equal to 137.15 and the activation energy  $E_a$  is 50.18 kJ/mol for binary Al-Si alloys.

## 5. Conclusions

An overarching and simple parameter able to fully quantify the effect of solutal on the grain size, independently of the nature of the alloy (i.e. wrought and shape-casting), is not available in the

solidification community. As demonstrated, the growth restriction factor  $Q$  is valid for *dilute alloy systems* but cannot properly quantify the solutal effect on *two-phase alloy systems* because the parameter  $m_L$  tends to zero as the eutectic point is reached. Under non-equilibrium solidification conditions, the maximum solubility of a particular solutal ( $C_{SM}$ ) is shifted to higher concentration ( $C_{SM}^*$ ). In the case of cast Al-Si alloys, this is experimentally found to be  $C_{SM}^* = 1.8 \cdot C_{SM}$ . Caution must be taken when comparing experimental data as the actual superheating, that is intrinsically dependent on the total amount of solutal, has also a significant influence on the final cast structure.

## Acknowledgments

The authors want to acknowledge the financial support from the Engineering and Physical Sciences Research Council (EPSRC) through the EP/J013749/1 and EP/K031422/1 Projects and from the Technology Strategy Board (TSB) through the TSB/101177 Project.

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